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H01M 4/58**H01M 4/02****H01M 10/40**(21)Application number : **09-327909**(71)Applicant : **SHARP CORP**(22)Date of filing : **28.11.1997**(72)Inventor : **MORI MOTOO
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KASAHARA MICHIO****(54) NONAQUEOUS SECONDARY BATTERY AND MANUFACTURE THEREOF**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an electrode enabling increase in the capacity and has excellent repetitive charging/discharging characteristics by using, as an electrode material, such an object as not including high crystallinity carbon having a highly oriented graphite structure but having a slightly disturbed layer structure in its laminate structure, or using carbon having a selective orientation.

SOLUTION: The disturbed layer structure or selective orientability is such one as having interlayer interval of the carbon planes found by X-ray diffraction method is in a range from 3.37 to 3.55 \AA , and not an object like graphite showing a sharp peak, but showing considerably broad diffraction peak. Furthermore, the peak intensity ratio of 1360 cm^{-1} to the peak intensity 1580 cm^{-1} of laser Raman spectrum is assigned to a range from 0.4 to 1.0. In this way, carbon body having wider plane interval, smaller crystallites and mutual orientability to some extent exhibits excellent characteristics as an electrode material. Such a body can be formed by a vapor phase deposition method by means of thermal decomposition on a substrate using a hydrocarbon or a hydrocarbon compound as a starting raw material.

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CLAIMS

[Claim(s)]

[Claim 1] The non-drainage system rechargeable battery with which the average spacing of the hex-stee side of a graphite is characterized by using for a negative electrode the electrode which makes a principal component the carbon material which has some random layer structure in the layer structure to which the ratio of the peak intensity of 1360cm-1 to the peak intensity of 1580cm-1 in 3.37A or 3.55A, and an argon laser Raman spectrum is expressed or less [0.4 or more] with 1.0.

[Claim 2] The ratio of the peak intensity of 1360cm-1 to the peak intensity [in / 3.37A or 3.55A, and an argon laser Raman spectrum / in the average spacing of the hex-stee side of a graphite] of 1580cm-1 has some random layer structure in the layer structure expressed or less / 0.4 or more / with 1.0. The non-drainage system rechargeable battery with which the relative inclination of C shaft orientations between each microcrystal is characterized by using for a negative electrode the electrode which makes a principal component the carbon material which has an alternative stacking tendency **75 degrees or less by the diffraction pattern of the field in a reflective high-speed electron diffraction (002).

[Claim 3] The manufacture method of the non-drainage system rechargeable battery characterized by using for a negative electrode the electrode which supplies the hydrocarbon compound which added or replaced the characteristic group containing at least one or more elements chosen as some of hydrocarbons or hydrocarbons from oxygen, nitrogen, sulfur, or the halogen to the system of reaction, and makes the carbon-deposit object by the pyrolysis by which gaseous-phase deposition was carried out an electrode active material within this system of reaction.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] Especially this invention relates to the electrode active material of the cell which uses as the dopant matter the electrode active material of the cell which uses alkali metal, such as a lithium (Li) and a potassium (K), alkaline earth metal, the rare earth metal, or transition metals as the dopant matter or a halogen, a halogenated compound, and an oxygen acid about a non-drainage system rechargeable battery and its manufacture method.

[0002]

[Description of the Prior Art] In recent years, the research which is going to apply a carbon material to the electrode of a cell is active.

[0003] For example, activated carbon or an activated carbon fiber is used for a positive electrode, a graphite or graphitized-carbon fiber is used for a negative electrode, and the cell in which charge and discharge are possible using the organic material as the electrolytic solution is indicated by JP,60-182670,A.

[0004] Moreover, it is the shape of annual rings to a fiber axis substantially [a carbonaceous hex-steel flat surface] in parallel with JP,60-20466,A. There is a publication about the cell active material containing the nickel chloride graphite lamellar compound of the graphite fiber which heat-treats the carbon fiber which has the organization which arranged, and is obtained.

[0005] Furthermore, the rechargeable battery which used the carbon fiber structure is indicated by JP,60-36315,A.

[0006]

[Problem(s) to be Solved by the Invention] Now, although the hex-steel side which a carbon atom makes arranges regularly the graphite used as an electrode material and it is called graphite structure, this has the layer structure to which the laminating of the carbon layer of a hex-steel side was carried out in parallel. Although the high thing of the regularity of this layer structure is called graphite, when only calling it a carbon material, what continues very broadly to that by which the carbon atom was arranged by high regularity like a graphite from what has the completely irregular layer structure called the non-fixed form carbon like activated carbon is known.

[0007] However, it is thought that the graphite material for now using as an electrode material must be a crystalline high material.

[0008] That is, in the case of above-mentioned JP,60-182670,A, the ratio of the peak intensity which appears in 1350cm⁻¹ and 1580cm⁻¹ in the Raman spectrum by Ar-ion-laser light uses the crystalline high high graphitized-carbon object or less of 0.4. Similarly, in the case of JP,60-36315,A, this crystalline demand is still higher, and the ratio of the Raman intensity of 1360cm⁻¹ to the Raman intensity of 1580cm⁻¹ uses the very high graphitized-carbon layer of 1/10 for it.

[0009] Moreover, graphitization processing is carried out at the elevated temperature of 2700-3000 degrees C for the carbon fiber which was grown up on the substrate in the case of JP,60-20466,A, a graphite microcrystal is grown up further, and high graphitization fiber is obtained and used.

[0010] Thus, although it is now believed generally that high crystallinity is required for the graphite as an electrode material, in the case of the graphite which has perfect crystallinity, the interlayer spacing is comparatively as narrow as 3.354Å. However, in the case of a high graphitized-carbon object (crystalline high graphite material), although the dopant matter will go in and out between this layer when a graphite is used, in order to form an intercalation compound as an electrode material, since the laminating of the hex-steel side was carried out to the top where an interlayer spacing is narrow very regularly as mentioned above, there was a problem that the amount by which the dopant matter is doped in near ordinary temperature decreased.

[0011] Then, this invention aims at offering the electrode which is made in view of the above-mentioned trouble, and has remarkable big electric capacity compared with the conventional carbon material, and was excellent in the charge-and-discharge repeat property, and its manufacture method.

[0012]

[Means for Solving the Problem] the carbon (crystalline high carbon) which has the graphite structure which carried out orientation highly as a result of an invention-in-this-application person's repeating research wholeheartedly, in order to attain the above-mentioned purpose -- not but The knowledge that electric capacity was large compared with the conventional thing, and the electrode excellent in the charge-and-discharge repeat property could be obtained was able to be acquired by using for the layer structure the thing which gave few random layer structures, or the carbon which gave the alternative stacking tendency as an electrode material. If the random layer structure of this carbon material or the grade of an alternative stacking tendency is

expressed objective, it will become as follows.

[0013] Namely, the thing which the interlayer spacing of the carbon flat surface by the X-ray diffraction method is not 3.37Å - 3.55Å, does not show a sharp peak like a graphite, and shows a quite broad diffraction peak.

[0014] Furthermore, the peak intensity ratio of 1360cm⁻¹ to the peak intensity of 1580cm⁻¹ of a laser Raman spectrum is or more 0.4 1.0 or less thing.

[0015] Although each physical-properties value is common knowledge as a physical-properties value showing a degree of graphitization, the physical properties of material can be expressed by combining the physical-properties value acquired from Raman scattering, and the physical-properties value acquired from an X diffraction. As everyone knows, the physical-properties value acquired from Raman scattering is the information on the about 50nm front face of a pole from the front face of a carbon material, and the physical-properties value acquired from an X diffraction is the information as an average to a certain amount of depth including the front face of about dozens of micrometers. That is, the structure of the depth direction can be grasped by combining these two physical-properties values.

[0016] Moreover, it is admitted that its size of the microcrystal of ab shaft orientations is very small since the size of the microcrystal for which it asked from the diffraction full width at half maximum is very broadcloth even if the size of the microcrystal of the diffraction peak of a field (002) to C shaft orientations is not 20Å - 1000Å, and the diffraction peak of a field (110) hardly appears or it appears. In addition, a reflection-electron line diffraction pattern has the shape of a broadcloth ring, and the microcrystal is reflecting the very fine thing. These rings are equivalent to (002) of graphite structure, (004), and reflection (006). Moreover, envelopment of each microcrystal is a thing within the limits whose relative inclination of C shaft orientations between each microcrystal it is not random, the field (001.) of each microcrystal has gathered in the specific direction, and is **75 degrees.

[0017] Thus, compared with a high graphitized-carbon object, a spacing is large, the size of a microcrystal is small, and the carbon body which has a certain amount of stacking tendency mutually shows a property good as an electrode material.

[0018] The carbon body which has the above property can be obtained by the following manufacture methods. That is, this can be supplied to the system of reaction by the ability using a hydrocarbon or a hydrocarbon compound as a start raw material, and it can form in up to a substrate by the gaseous-phase depositing method by the pyrolysis.

[0019] What added or replaced the characteristic group containing at least one or more elements chosen as some hydrocarbons from oxygen, nitrogen, sulfur, or the halogen as a hydrocarbon compound can be used.

[0020] If an above-mentioned carbon material is used for the electrode of the cell which alkali metal etc. contained as dopant matter, the dope of the dopant matter and a ** dope will tend to take place compared with the conventional high graphitized-carbon object, and electric capacity will become large. Moreover, since an above-mentioned carbon body can carry out direct formation to up to a substrate as a thin film, the utilization factor of an active material becomes [internal resistance] small highly. Moreover, since it is producible in arbitrary configurations, it is effective in thin form-ization of an electrode etc. being attained.

[0021]

[Embodiments of the Invention]

(Example 1) Hereafter, with reference to a drawing, one example is given and this invention is explained in detail.

[0022] Drawing 1 is an X diffraction view which uses as the light source CuKalpha of the carbon body used for the electrode of the invention in this application. The formula of the black of this diffraction peak to a degree (several 1)

[0023]

[Equation 1]

$$d = \frac{\lambda}{2 \cdot \sin \theta} \quad (\lambda = 1.5418 \text{ \AA})$$

[0024] When it is alike and the average spacing of a field is searched for more (002), it is 3.45Å, and it is the following formula (several 2) from the peak-mesial-magnitude width of face beta.

[0025]

[Equation 2]

$$L_c = \frac{\kappa \cdot \lambda}{\beta \cdot \cos \theta} \quad (\lambda = 1.5418 \text{ \AA})$$

$$(\kappa = 0.9)$$

[0026] It was 27.2Å when asked more for the size of the microcrystal of C shaft orientations.

[0027] Moreover, drawing 2 is the Raman spectrum which used the argon laser of this carbon body. It is 0.8 when the peak intensity of 1360cm⁻¹ to the peak intensity of 1580cm⁻¹ is seen so that clearly from this drawing.

[0028] Moreover, when the diffraction photograph of an electron ray is searched for by the reflective high-speed electron-diffraction (RHEED) method (002), (004) and reflection (006) show the PURODO spot, the stacking tendency of each microcrystal is quite good, and the distribution of C shaft orientations is less than **18 degrees.

[0029] This carbon body (film in which the carbon material was formed on the substrate) was pinched in the network for current collection, and it considered as the electrode. Let this be the examination pole A. It arranged in the cell as shows the examination pole A to drawing 3, and the charge and discharge test by the dope and ** dope of a lithium element was performed by using a

lithium as the dopant matter, having used the lithium metal as the opposite solution. The lithium with which the electrode (examination pole A) which consists of a carbon body which 12 requires for the invention in this application in drawing 3, and 13 used the charge collector, and 14 used a counter electrode and 15 as a reference pole, the electrolytic solution which 16 becomes from the propylene carbonate which dissolved the one-mol fault hydrochloric-acid lithium, and 17 are cells.

[0030] Drawing 4 is a potential variation diagram to the lithium reference pole in 25 degrees C at the time of making various carbon materials dope and ** dope a lithium. The curve A of drawing 4 is a potential change curve of the electrode of the invention in this application. In Curve A, the direction where the direction where potential approaches 0V becomes a dope (charge) and a high voltage is a ** dope (electric discharge).

[0031] Drawing 5 shows change of the service capacity in the test to which the charge and discharge of the various carbon materials are carried out by the constant current between 0V and 2.5V to a lithium reference electrode. The curve A of drawing 5 is a curve which shows the electrode characteristic of the invention in this application. Most capacity degradation by the repeat of ***** cannot be found, and the repeat property is very good so that more clearly as a result.

[0032] As mentioned above, if the carbon body of the invention in this application is used, the negative electrode of the non-water lithium rechargeable battery in which charge and discharge are possible can be constituted.

[0033] Below, an example of the manufacture method of an above-mentioned carbon material is explained using a drawing.

[0034] Drawing 6 is the block block diagram of the carbon-material generation equipment used for manufacture of the carbon material used for the electrode of the invention in this application.

[0035] as the hydrocarbon compound which contained in part the hydrocarbon used as a starting material, and various characteristic groups -- for example, aliphatic hydrocarbon -- there are a unsaturated hydrocarbon, an aromatic compound, and an alicyclic compound preferably These are pyrolyzed at 1000 degrees C. Specifically, acetylene, diphenyl, acetylene, acrylonitrile, 1,2-dibromo ethylene, 2-butyne, benzene, toluene, a pyridine, an aniline, a phenol, diphenyl, an anthracene, a pyrene, a HIKISA methylbenzene, styrene, allyl-compound benzene, a cyclohexane, a normal hexane, a pyrrole, a thiophene, etc. are raised.

[0036] The supply method to the coil mentioned later is controlled by the kind of used hydrocarbon compound by the amount of supply below the number millimole of per hour using the bubbler method, the evaporating method, or the sublimating method. If many amount of supply is taken, a soot-like carbon-deposit object will be generated and a carbon material required for the electrode composition of this invention will not be obtained. The substrate which is deposited by the carbon material and generated does not need to deteriorate in the reaction temperature of about 1000 degrees C.

[0037] Hereafter, it explains according to a manufacturing process.

[0038] In the bubble container 1 with which the benzene which performed refining operation by vacuum distillation was contained, from the argon gas-control system 2, argon gas is supplied, the bubble of the benzene is carried out, and the quartz coil 4 is fed with a benzene molecule through the Pyrex-glass pipe 3. Under the present circumstances, the temperature of the liquid benzene in the bubble container 1 is held uniformly, an argon quantity of gas flow is adjusted by the bubble 5, and the amount of supply into the coil 4 of a benzene molecule is controlled to the number millimole of per hour. The benzene number density of molecules and the rate of flow in the argon gas in the glass tube 3 just before passing argon gas and feeding a coil 4 from the dilution line 6 on the other hand are optimized. The heating furnace 8 is formed in the periphery enclosure of a coil 4. The substrate for deposition generation in a coil 4 is held by this heating furnace 8 at the temperature of about 1000 degrees C.

[0039] If fed with a benzene molecule in a coil 4, a benzene molecule will be pyrolyzed within a coil 4 and a carbon-deposit object will be generated on a substrate. The gas into a coil 4 is introduced through an exhaust pipe 9 to the exhaust air system 10, and is removed from a coil 4. The benzene molecule introduced in the coil 4 is heated at the temperature of about 1000 degrees C, and is pyrolyzed, and growth formation is carried out one by one on a substrate. In this case, the carbon which grows serves as a thin film with metallic luster, and since a reaction is advanced at low temperature compared with the method of forming graphite material by process like before, a carbon material with a good matter value can be manufactured. In addition, if it is this method, an anisotropy etc. is arbitrarily controllable by selecting the amount of supply of a starting material and a starting material, a speed of supply, and reaction temperature.

[0040] (Example 2) Many properties of the carbon film of the 2nd example are as follows. That is, the average spacing of a field (002) was 3.37A as shown in drawing 7, and the peak intensity ratio of 1360cm-1 to the peak intensity of 1580cm-1 by the Raman spectrum was 0.50 as shown in drawing 8. Moreover, the distribution of c shaft orientations of each microcrystal by the reflective high-speed electron diffraction was less than **60 degrees.

[0041] Lead wire was taken out from this carbon film formed on the substrate, and it considered as the electrode, and considered as the examination pole B. The lithium was used as the dopant matter for this by the same method as an example 1, and the charge-and-discharge test by the dope and the ** dope was performed. The curve B of drawing 4 is a potential change curve of the carbon material by this example. Moreover, the curve B of drawing 5 shows change of the service capacity in the repeat test of the carbon material by this example. Service capacity and a repeat property are very good so that more clearly as a result.

[0042] In addition, although the one-mol lithium perchlorate was used for the electrolyte and propylene carbonate was used for the electrolytic solution in this example It is not necessary to limit to this. as other electrolytes 6 fluoride lithium sulfate, There are hoe lithium fluoride, a truffe RUORO sulfonic-acid lithium, etc. as the electrolytic solution A dimethyl sulfoxide, organic solvents and water, such as gamma-butyl lactone, a sulfolane tetrahydrofuran, 2-methyl tetrahydrofuran, 1,2-dimethoxyethane, and a 1,3-dioxolane, are raised, and independent in these -- or it can mix and use

[0043] (Example 1 of comparison) The invention in this application is compared about the graphitized-carbon object which heat-treated it at 2800 degrees C after stripping off from a substrate the carbon body made to deposit at 1200 degrees C on a

quartz substrate.

[0044] The X diffraction data of this carbon body are shown in drawing 9. The spacing of the field (002) of this carbon body was 3.36Å. Moreover, in the Raman spectrum, the peak intensity ratio of 1360cm⁻¹ to the peak intensity of 1580cm⁻¹ was 0.1 (drawing 10). This carbon body was used as the electrode by the same method as an example 1, and it considered as the examination pole C. It arranged in the cell as shows the examination pole C to drawing 3, and the charge-and-discharge test was performed like the example 1. The curve c of drawing 4 is a potential change curve of the carbon material by this example of comparison. Compared with the electrode of the above-mentioned examples 1 and 2, service capacity was also slight and more unsuitable than this result as an electrode material.

[0045] (Example 2 of comparison) The petroleum coke which is not refined having removed the volatile component from the crude oil was heat-treated at 500 degrees C. A bodily X diffraction view is shown in drawing 11 in this end of a carbon powder. The average spacing of a field (002) was 3.45Å from this diffraction peak. Moreover, in the Raman spectrum, the peak intensity ratio of 1360cm⁻¹ to the peak intensity of 1580cm⁻¹ was 0.8. This result is shown in drawing 12. Moreover, according to the diffraction pattern in the electrode which pressed this carbon body by the reflective high-speed electron diffraction, and was obtained, it became clear that each ring of a diffraction pattern becomes uniform and does not have a stacking tendency. The letter nickel substrate of foaming was filled up with this carbon body, and what was pressed was used as the electrode and it considered as the examination pole D. It arranged in the cell as shows the examination pole D to drawing 3, and the charge-and-discharge test was performed like the example 1. The curve D of drawing 4 is a potential curve of the carbon material by this example of comparison. There is less service capacity than this result compared with the above-mentioned examples 1 and 2. However, the initial charge-and-discharge property was good compared with the example 1 of comparison.

[0046] By the same method as an example 1, the repeat test of charge and discharge was performed for the examination pole D. The curve D of drawing 5 shows the result depended on this example of comparison. Degradation of capacity produces what does not have the stacking tendency of each microcrystal in an electrode from this result by the repeat of charge and discharge, and an intolerable thing is accepted in long-term use.

[0047]

[Effect of the Invention] According to the invention in this application, the dope of the dopant matter and a ** dope tend to take place compared with the conventional high graphitized-carbon object, and electric capacity becomes large. Moreover, since an above-mentioned carbon body can carry out direct formation to up to a substrate as a thin film, the utilization factor of an active material becomes [internal resistance] small highly. Moreover, since it is producible in arbitrary configurations, there is a remarkable effect that thin form-ization of an electrode etc. is attained.

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TECHNICAL FIELD

[The technical field to which invention belongs] Especially this invention relates to the electrode active material of the cell which uses as the dopant matter the electrode active material of the cell which uses alkali metal, such as a lithium (Li) and a potassium (K), alkaline earth metal, a rare earth metal, or transition metals as the dopant matter or a halogen, a halogenated compound, and an oxygen acid about a non-drainage system rechargeable battery and its manufacture method.

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PRIOR ART

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[0003] For example, activated carbon or an activated carbon fiber is used for a positive electrode, a graphite or graphitized-carbon fiber is used for a negative electrode, and the cell in which charge and discharge are possible using the organic material as the electrolytic solution is indicated by JP,60-182670,A.

[0004] Moreover, it is the shape of annual rings to a fiber axis substantially [a carbonaceous hex-steel flat surface] in parallel with JP,60-20466,A. There is a publication about the cell active material containing the nickel chloride graphite lamellar compound of the graphite fiber which heat-treats the carbon fiber which has the organization which arranged, and is obtained.

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EFFECT OF THE INVENTION

[Effect of the Invention] According to the invention in this application, the dope of the dopant matter and a ** dope tend to take place compared with the conventional high graphitized-carbon object, and electric capacity becomes large. Moreover, since an above-mentioned carbon body can carry out direct formation to up to a substrate as a thin film, the utilization factor of an active material becomes [internal resistance] small highly. Moreover, since it is producible in arbitrary configurations, there is a remarkable effect that thin form-ization of an electrode etc. is attained.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Now, although the hex-steel side which a carbon atom makes arranges regularly the graphite used as an electrode material and it is called graphite structure, this has the layer structure to which the laminating of the carbon layer of a hex-steel side was carried out in parallel. Although the high thing of the regularity of this layer structure is called graphite, when only calling it a carbon material, what continues very broadly to that by which the carbon atom was arranged by high regularity like a graphite from what has the completely irregular layer structure called the non-fixed form carbon like activated carbon is known.

[0007] However, it is thought that the graphite material for now using as an electrode material must be a crystalline high material.

[0008] That is, in the case of above-mentioned JP,60-182670,A, the ratio of the peak intensity which appears in 1350cm⁻¹ and 1580cm⁻¹ in the Raman spectrum by Ar-ion-laser light uses the crystalline high high graphitized-carbon object or less of 0.4. Similarly, in the case of JP,60-36315,A, this crystalline demand is still higher, and the ratio of the Raman intensity of 1360cm⁻¹ to the Raman intensity of 1580cm⁻¹ uses the very high graphitized-carbon layer of 1/10 for it.

[0009] Moreover, graphitization processing is carried out at the elevated temperature of 2700-3000 degrees C for the carbon fiber which was grown up on the substrate in the case of JP,60-20466,A, a graphite microcrystal is grown up further, and high graphitization fiber is obtained and used.

[0010] Thus, although it is now believed generally that high crystallinity is required for the graphite as an electrode material, in the case of the graphite which has perfect crystallinity, the interlayer spacing is comparatively as narrow as 3.354A. However, in the case of a high graphitized-carbon object (crystalline high graphite material), although the dopant matter will go in and out between this layer when a graphite is used, in order to form an intercalation compound as an electrode material, since the laminating of the hex-steel side was carried out to the top where an interlayer spacing is narrow very regularly as mentioned above, there was a problem that the amount by which the dopant matter is doped in near ordinary temperature decreased.

[0011] Then, this invention aims at offering the electrode which is made in view of the above-mentioned trouble, and has remarkable big electric capacity compared with the conventional carbon material, and was excellent in the charge-and-discharge repeat property, and its manufacture method.

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MEANS

[Means for Solving the Problem] the carbon (crystalline high carbon) which has the graphite structure which carried out orientation highly as a result of an invention-in-this-application person's repeating research wholeheartedly, in order to attain the above-mentioned purpose -- not but The knowledge that electric capacity was large compared with the conventional thing, and the electrode excellent in the charge-and-discharge repeat property could be obtained was able to be acquired by using for the layer structure the thing which gave few random layer structures, or the carbon which gave the alternative stacking tendency as an electrode material. If the random layer structure of this carbon material or the grade of an alternative stacking tendency is expressed objective, it will become as follows.

[0013] Namely, the thing which the interlayer spacing of the carbon flat surface by the X-ray diffraction method is not 3.37 Å - 3.55 Å, does not show a sharp peak like a graphite, and shows a quite broad diffraction peak.

[0014] Furthermore, the peak intensity ratio of 1360cm⁻¹ to the peak intensity of 1580cm⁻¹ of a laser Raman spectrum is or more 0.4 1.0 or less thing.

[0015] Although each physical-properties value is common knowledge as a physical-properties value showing a degree of graphitization, the physical properties of material can be expressed by combining the physical-properties value acquired from Raman scattering, and the physical-properties value acquired from an X diffraction. As everyone knows, the physical-properties value acquired from Raman scattering is the information on the about 50nm front face of a pole from the front face of a carbon material, and the physical-properties value acquired from an X diffraction is the information as an average to a certain amount of depth including the front face of about dozens of micrometers. That is, the structure of the depth direction can be grasped by combining these two physical-properties values.

[0016] Moreover, it is admitted that its size of the microcrystal of ab shaft orientations is very small since the size of the microcrystal for which it asked from the diffraction full width at half maximum is very broadcloth even if the size of the microcrystal of the diffraction peak of a field (002) to C shaft orientations is not 20 Å - 1000 Å, and the diffraction peak of a field (110) hardly appears or it appears. In addition, a reflection-electron line diffraction pattern has the shape of a broadcloth ring, and the microcrystal is reflecting the very fine thing. These rings are equivalent to (002) of graphite structure, (004), and reflection (006). Moreover, envelopment of each microcrystal is a thing within the limits whose relative inclination of C shaft orientations between each microcrystal it is not random, the field (001.) of each microcrystal has gathered in the specific direction, and is **75 degrees.

[0017] Thus, compared with a high graphitized-carbon object, a spacing is large, the size of a microcrystal is small, and the carbon body which has a certain amount of stacking tendency mutually shows a property good as an electrode material.

[0018] The carbon body which has the above property can be obtained by the following manufacture methods. That is, this can be supplied to the system of reaction by the ability using a hydrocarbon or a hydrocarbon compound as a start raw material, and it can form in up to a substrate by the gaseous-phase depositing method by the pyrolysis.

[0019] What added or replaced the characteristic group containing at least one or more elements chosen as some hydrocarbons from oxygen, nitrogen, sulfur, or the halogen as a hydrocarbon compound can be used.

[0020] If an above-mentioned carbon material is used for the electrode of the cell which alkali metal etc. contained as dopant matter, the dope of the dopant matter and a ** dope will tend to take place compared with the conventional high graphitized-carbon object, and electric capacity will become large. Moreover, since an above-mentioned carbon body can carry out direct formation to up to a substrate as a thin film, the utilization factor of an active material becomes [internal resistance] small highly. Moreover, since it is producible in arbitrary configurations, it is effective in thin form-ization of an electrode etc. being attained.

[0021]

[Embodiments of the Invention]

(Example 1) Hereafter, with reference to a drawing, one example is given and this invention is explained in detail.

[0022] Drawing 1 is an X diffraction view which uses as the light source CuKalpha of the carbon body used for the electrode of the invention in this application. The formula of the black of this diffraction peak to a degree (several 1)

[0023]

[Equation 1]

$$d = \frac{\lambda}{2 \cdot \sin \theta} \quad (\lambda = 1.5418 \text{ Å})$$

[0024] When it is alike and the average spacing of a field is searched for more (002), it is 3.45Å, and it is the following formula (several 2) from the peak-mesial-magnitude-width of face beta.

[0025]

[Equation 2]

$$L_c = \frac{\kappa \cdot \lambda}{\beta \cdot \cos \theta} \quad (\lambda = 1.5418 \text{ \AA})$$

$$(\kappa = 0.9)$$

[0026] It was 27.2Å when asked more for the size of the microcrystal of C shaft orientations.

[0027] Moreover, drawing 2 is the Raman spectrum which used the argon laser of this carbon body. It is 0.8 when the peak intensity of 1360cm⁻¹ to the peak intensity of 1580cm⁻¹ is seen so that clearly from this drawing.

[0028] Moreover, when the diffraction photograph of an electron ray is searched for by the reflective high-speed electron-diffraction (RHEED) method (002), (004) and reflection (006) show the PURODO spot, the stacking tendency of each microcrystal is quite good, and the distribution of C shaft orientations is less than **18 degrees.

[0029] This carbon body (film in which the carbon material was formed on the substrate) was pinched in the network for current collection, and it considered as the electrode. Let this be the examination pole A. It arranged in the cell as shows the examination pole A to drawing 3, and the charge and discharge test by the dope and ** dope of a lithium element was performed by using a lithium as the dopant matter, having used the lithium metal as the opposite solution. The lithium with which the electrode (examination pole A) which consists of a carbon body which 12 requires for the invention in this application in drawing 3, and 13 used the charge collector, and 14 used a counter electrode and 15 as a reference pole, the electrolytic solution which 16 becomes from the propylene carbonate which dissolved the one-mol fault hydrochloric-acid lithium, and 17 are cells.

[0030] Drawing 4 is a potential variation diagram to the lithium reference pole in 25 degrees C at the time of making various carbon materials dope and ** dope a lithium. The curve A of drawing 4 is a potential change curve of the electrode of the invention in this application. In Curve A, the direction where the direction where potential approaches 0V becomes a dope (charge) and a high voltage is a ** dope (electric discharge).

[0031] Drawing 5 shows change of the service capacity in the test to which the charge and discharge of the various carbon materials are carried out by the constant current between 0V and 2.5V to a lithium reference electrode. The curve A of drawing 5 is a curve which shows the electrode characteristic of the invention in this application. Most capacity degradation by the repeat of ***** cannot be found, and the repeat property is very good so that more clearly as a result.

[0032] As mentioned above, if the carbon body of the invention in this application is used, the negative electrode of the non-water lithium rechargeable battery in which charge and discharge are possible can be constituted.

[0033] Below, an example of the manufacture method of an above-mentioned carbon material is explained using a drawing.

[0034] Drawing 6 is the block block diagram of the carbon-material generation equipment used for manufacture of the carbon material used for the electrode of the invention in this application.

[0035] as the hydrocarbon compound which contained in part the hydrocarbon used as a starting material, and various characteristic groups -- for example, aliphatic hydrocarbon -- there are a unsaturated hydrocarbon, an aromatic compound, and an alicyclic compound preferably These are pyrolyzed at 1000 degrees C. Specifically, acetylene, diphenyl, acetylene, acrylonitrile, 1,2-dibromo ethylene, 2-butyne, benzene, toluene, a pyridine, an aniline, a phenol, diphenyl, an anthracene, a pyrene, a HIKISA methylbenzene, styrene, allyl-compound benzene, a cyclohexane, a normal hexane, a pyrrole, a thiophene, etc. are raised.

[0036] The supply method to the coil mentioned later is controlled by the kind of used hydrocarbon compound by the amount of supply below the number millimole of per hour using the bubbler method, the evaporating method, or the sublimating method. If many amount of supply is taken, a soot-like carbon-deposit object will be generated and a carbon material required for the electrode composition of this invention will not be obtained. The substrate which is deposited by the carbon material and generated does not need to deteriorate in the reaction temperature of about 1000 degrees C.

[0037] Hereafter, it explains according to a manufacturing process:

[0038] In the bubble container 1 with which the benzene which performed refining operation by vacuum distillation was contained, from the argon gas-control system 2, argon gas is supplied, the bubble of the benzene is carried out, and the quartz coil 4 is fed with a benzene molecule through the Pyrex-glass pipe 3. Under the present circumstances, the temperature of the liquid-benzene in the bubble container 1 is held uniformly, an argon quantity of gas flow is adjusted by the bubble 5, and the amount of supply into the coil 4 of a benzene molecule is controlled to the number millimole of per hour. The benzene number density of molecules and the rate of flow in the argon gas in the glass tube 3 just before passing argon gas and feeding a coil 4 from the dilution line 6 on the other hand are optimized. The heating furnace 8 is formed in the periphery enclosure of a coil 4. The substrate for deposition generation in a coil 4 is held by this heating furnace 8 at the temperature of about 1000 degrees C.

[0039] If fed with a benzene molecule in a coil 4, a benzene molecule will be pyrolyzed within a coil 4 and a carbon-deposit object will be generated on a substrate. The gas into a coil 4 is introduced through an exhaust pipe 9 to the exhaust air system 10, and is removed from a coil 4. The benzene molecule introduced in the coil 4 is heated at the temperature of about 1000 degrees C, and is pyrolyzed, and growth formation is carried out one by one on a substrate. In this case, the carbon which grows serves as a thin film with metallic luster, and since a reaction is advanced at low temperature compared with the method of forming graphite material by process like before, a carbon material with a good matter value can be manufactured. In addition, if it is this method, an anisotropy etc. is arbitrarily controllable by selecting the amount of supply of a starting material and a starting material, a speed

of supply, and reaction temperature.

[0040] (Example 2) Many properties of the carbon film of the 2nd example are as follows. That is, the average spacing of a field (002) was 3.37Å as shown in drawing 7, and the peak intensity ratio of 1360cm⁻¹ to the peak intensity of 1580cm⁻¹ by the Raman spectrum was 0.50 as shown in drawing 8. Moreover, the distribution of c shaft orientations of each microcrystal by the reflective high-speed electron diffraction was less than **60 degrees.

[0041] Lead wire was taken out from this carbon film formed on the substrate, and it considered as the electrode, and considered as the examination pole B. The lithium was used as the dopant matter for this by the same method as an example 1, and the charge-and-discharge test by the dope and the ** dope was performed. The curve B of drawing 4 is a potential change curve of the carbon material by this example. Moreover, the curve B of drawing 5 shows change of the service capacity in the repeat test of the carbon material by this example. Service capacity and a repeat property are very good so that more clearly as a result.

[0042] In addition, although the one-mol lithium perchlorate was used for the electrolyte and propylene carbonate was used for the electrolytic solution in this example It is not necessary to limit to this. as other electrolytes 6 fluoride lithium sulfate, There are hoe lithium fluoride, a truffle RUORO sulfonic-acid lithium, etc. as the electrolytic solution A dimethyl sulfoxide, organic solvents and water, such as gamma-butyl lactone, a sulfolane tetrahydrofuran, 2-methyl tetrahydrofuran, 1,2-dimethoxyethane, and a 1,3-dioxolane, are raised, and independent in these -- or it can mix and use

[0043] (Example 1 of comparison) The invention in this application is compared about the graphitized-carbon object which heat-treated it at 2800 degrees C after stripping off from a substrate the carbon body made to deposit at 1200 degrees C on a quartz substrate.

[0044] The X diffraction data of this carbon body are shown in drawing 9. The spacing of the field (002) of this carbon body was 3.36Å. Moreover, in the Raman spectrum, the peak intensity ratio of 1360cm⁻¹ to the peak intensity of 1580cm⁻¹ was 0.1 (drawing 10). This carbon body was used as the electrode by the same method as an example 1, and it considered as the examination pole C. It arranged in the cell as shows the examination pole C to drawing 3, and the charge-and-discharge test was performed like the example 1. The curve c of drawing 4 is a potential change curve of the carbon material by this example of comparison. Compared with the electrode of the above-mentioned examples 1 and 2, service capacity was also slight and more unsuitable than this result as an electrode material.

[0045] (Example 2 of comparison) The petroleum coke which is not refined having removed the volatile component from the crude oil was heat-treated at 500 degrees C. A bodily X diffraction view is shown in drawing 11 in this end of a carbon powder. The average spacing of a field (002) was 3.45Å from this diffraction peak. Moreover, in the Raman spectrum, the peak intensity ratio of 1360cm⁻¹ to the peak intensity of 1580cm⁻¹ was 0.8. This result is shown in drawing 12. Moreover, according to the diffraction pattern in the electrode which pressed this carbon body by the reflective high-speed electron diffraction, and was obtained, it became clear that each ring of a diffraction pattern becomes uniform and does not have a stacking tendency. The letter nickel substrate of foaming was filled up with this carbon body, and what was pressed was used as the electrode and it considered as the examination pole D. It arranged in the cell as shows the examination pole D to drawing 3, and the charge-and-discharge test was performed like the example 1. The curve D of drawing 4 is a potential curve of the carbon material by this example of comparison. There is less service capacity than this result compared with the above-mentioned examples 1 and 2. However, the initial charge-and-discharge property was good compared with the example 1 of comparison.

[0046] By the same method as an example 1, the repeat test of charge and discharge was performed for the examination pole D. The curve D of drawing 5 shows the result depended on this example of comparison. Degradation of capacity produces what does not have the stacking tendency of each microcrystal in an electrode from this result by the repeat of charge and discharge, and an intolerable thing is accepted in long-term use.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the X diffraction view of the carbon material of this invention.

[Drawing 2] It is drawing showing the Raman spectrum of the carbon material of this invention.

[Drawing 3] It is the schematic diagram of the equipment for electrode characteristic measurement of the carbon material of this invention.

[Drawing 4] It is the charge-and-discharge property view of the carbon material of this invention, and the existing carbon material.

[Drawing 5] It is the cycle property view of the charge-and-discharge capacity of the carbon material of this invention, and the existing carbon material.

[Drawing 6] It is the block block diagram of the carbon-material generation equipment with which explanation of one example of this invention is presented.

[Drawing 7] It is the X diffraction view of the carbon material of this invention.

[Drawing 8] It is drawing showing the Raman spectrum of the carbon material of this invention.

[Drawing 9] It is the X diffraction view of the existing carbon material.

[Drawing 10] It is drawing showing the Raman spectrum of the existing carbon material.

[Drawing 11] It is the X diffraction view of the existing carbon material.

[Drawing 12] It is drawing showing the Raman spectrum of the existing carbon material.

[Description of Notations]

12 Examination Pole A

13 Charge Collector

14 Counter Electrode

15 Reference Pole

16 Electrolytic Solution

17 Cell

[Translation done.]

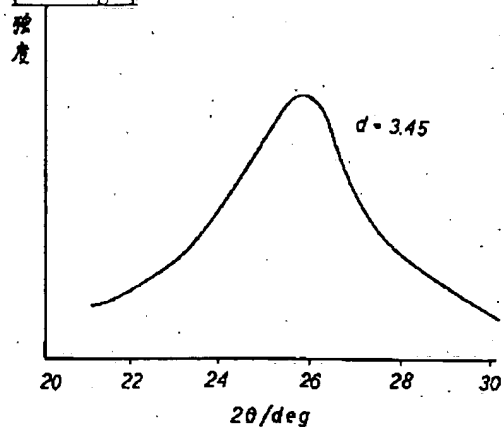
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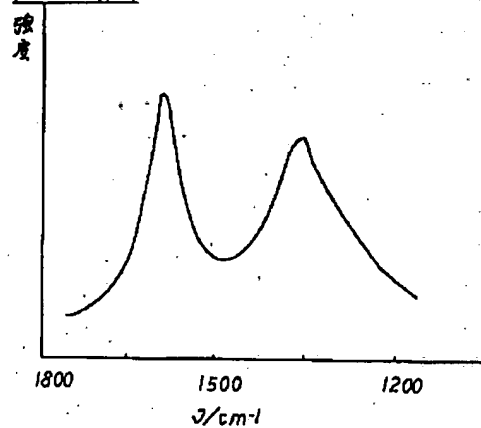
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DRAWINGS

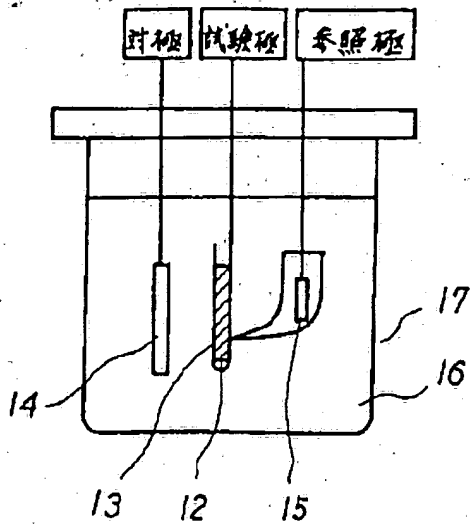
[Drawing 1]



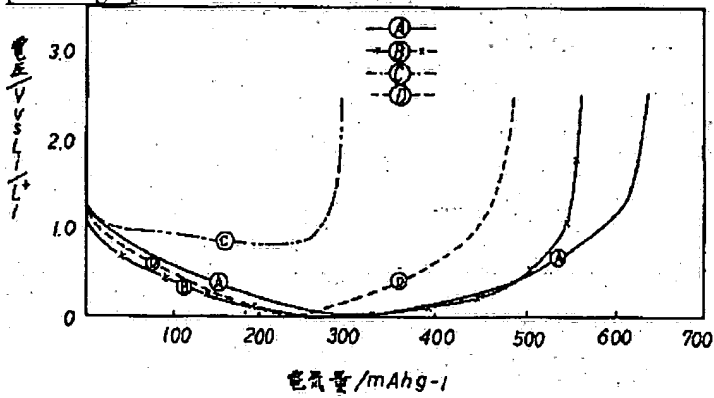
[Drawing 2]



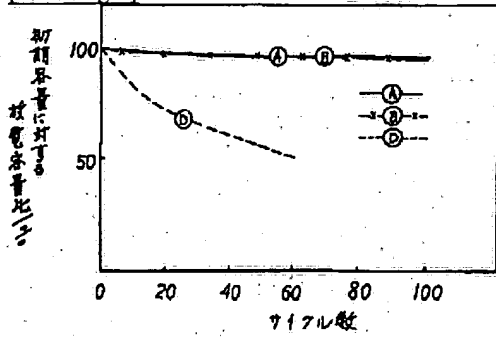
[Drawing 3]



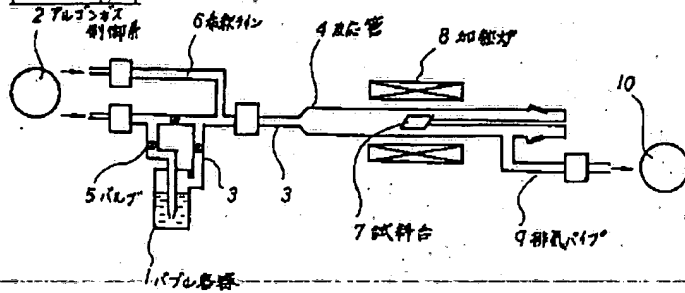
[Drawing 4]



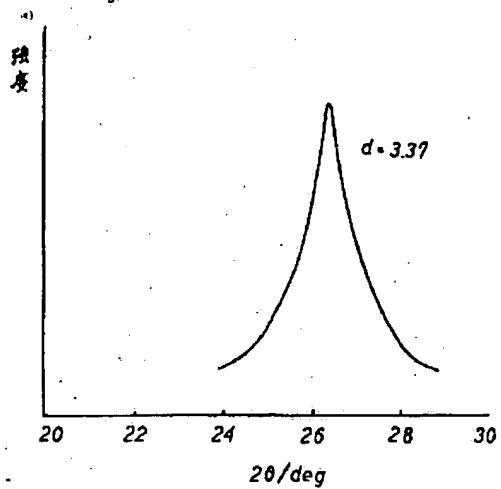
[Drawing 5]



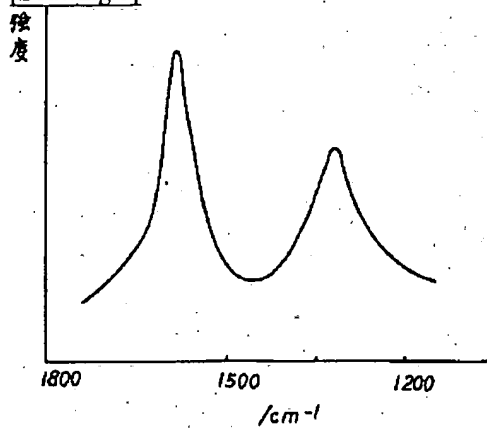
[Drawing 6]



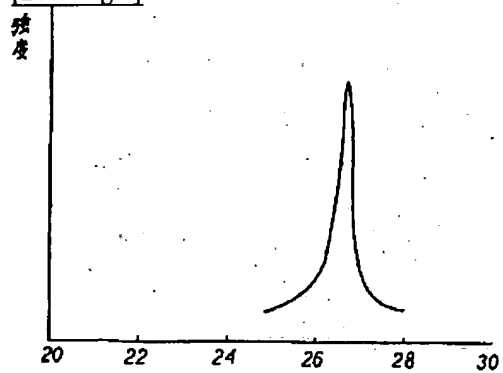
[Drawing 7]



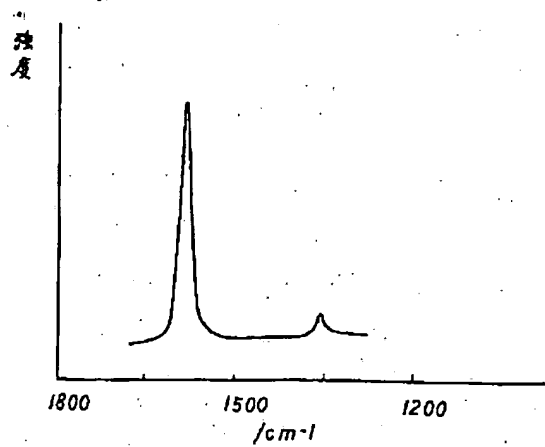
[Drawing 8]



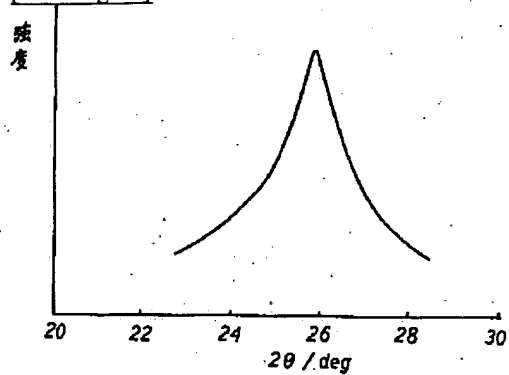
[Drawing 9]



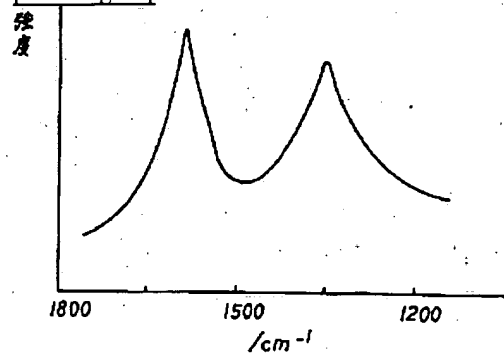
[Drawing 10]



[Drawing 11]



[Drawing 12]



[Translation done.]

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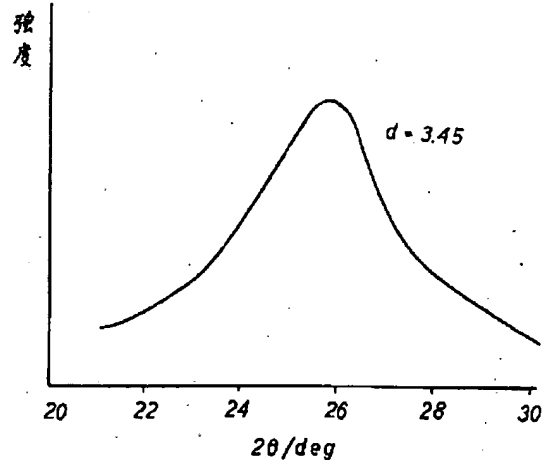
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(54) 【発明の名称】 非水系二次電池及びその製造方法

(57) 【要約】

【課題】 従来の炭素材料に比べて著しく大きな電気容量を有し、かつ充放電繰り返し特性の優れた非水系二次電池及びその製造方法を提供する。

【解決手段】 高度に配向した黒鉛構造を有する炭素（結晶性の高い炭素）ではなく、層状構造にわずかな乱層構造を持たせたもの、あるいは、選択的配向性を持たせた炭素を非水系二次電池の負極材料として用いる。



【特許請求の範囲】

【請求項1】 黒鉛の六角網面の平均面間隔が3.37 Å乃至3.55 Å、アルゴンレーザラマンスペクトルにおける1580 cm⁻¹のピーク強度に対する1360 cm⁻¹のピーク強度の比が0.4以上1.0以下で現される層構造に若干の乱層構造を有する炭素材料を主成分とする電極を負極に用いたことを特徴とする非水系二次電池。

【請求項2】 黒鉛の六角網面の平均面間隔が3.37 Å乃至3.55 Å、アルゴンレーザラマンスペクトルにおける1580 cm⁻¹のピーク強度に対する1360 cm⁻¹のピーク強度の比が0.4以上1.0以下で現される層構造に若干の乱層構造を有し、かつ、反射高速電子線回折における(002)面の回折図形で各結晶子間のC軸方向の相対的傾きが±75°以下の選択的配向性を有する炭素材料を主成分とする電極を負極に用いたことを特徴とする非水系二次電池。

【請求項3】 炭化水素または炭化水素の一部に酸素、窒素、硫黄もしくはハロゲンより選択された少なくとも1つ以上の元素を含む特性基を付加もしくは置換した炭化水素化合物を反応系へ供給し、該反応系内で熱分解による気相堆積された炭素堆積物を電極活物質とする電極を負極に用いたことを特徴とする非水系二次電池の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は非水系二次電池及びその製造方法に関し、特にリチウム(Li)やカリウム(K)等のアルカリ金属、アルカリ土類金属、希土類金属もしくは遷移金属をドーパント物質とする電池の電極活物質あるいはハロゲン、ハロゲン化合物、酸素酸をドーパント物質とする電池の電極活物質に関するものである。

【0002】

【従来の技術】近年、炭素材料を電池の電極に応用しようとする研究が活発である。

【0003】例えば、特開昭60-182670号公報には正極に活性炭あるいは活性炭素繊維を、負極に黒鉛あるいは黒鉛化炭素繊維を用い、電解液として有機材料を用いた充放電可能な電池が記載されている。

【0004】また、特開昭60-20466号公報には炭素の六角網平面が繊維軸に実質的に平行にかつ年輪状に配列した組織を有する炭素繊維を熱処理して得られる黒鉛繊維の塩化ニッケル黒鉛層間化合物を含む電池活物質に関する記載がある。

【0005】さらに、特開昭60-36315号公報には炭素繊維構造体を用いた二次電池が記載されている。

【0006】

【発明が解決しようとする課題】さて、電極材料として用いられる黒鉛は、炭素原子が作る六角網面が規則的に

配列したものであって黒鉛構造と称されるのであるが、これは六角網面の炭素層が平行に積層された層状構造を有している。この層状構造の規則性の高いものが黒鉛と呼ばれるのであるが、単に炭素材料という場合には活性炭のごとき無定型炭素と称される層状構造が全く不規則なものから、黒鉛のように高い規則性で炭素原子が配列されたものまで、極めて広範囲に亘るものが知られている。

【0007】しかしながら、現在のところ電極材料として用いるための黒鉛材料は結晶性の高い材料でなければならないと考えられている。

【0008】すなわち、上述の特開昭60-182670号公報の場合、アルゴンイオンレーザ光によるラマンスペクトルにおいて1350 cm⁻¹と1580 cm⁻¹とに現れるピーク強度の比率が0.4以下という結晶性の高い高黒鉛化炭素体を用いている。同様に、特開昭60-36315号公報の場合にはこの結晶性の要求はさらに高く、1580 cm⁻¹のラマン強度に対する1360 cm⁻¹のラマン強度の比が1/10という極めて高い黒鉛化炭素層を用いている。

【0009】また、特開昭60-20466号公報の場合には基板上に成長させた炭素繊維を2700~3000℃という高温で黒鉛化処理をして黒鉛結晶子を更に成長させて高黒鉛化繊維を得て使用している。

【0010】このように、現在のところ、一般に電極材料としての黒鉛には高い結晶性が必要であると信じられているのであるが、完全な結晶性を有する黒鉛の場合、その層間隔は3.354 Åと比較的狭い。ところが、電極材料として層間化合物を形成するために黒鉛を用いる場合、この層間にドーパント物質は出入りすることになるのであるが、高黒鉛化炭素体(結晶性の高い黒鉛材料)の場合、上述のように層間隔が狭い上に六角網面が非常に規則正しく積層されているため常温付近においてドーパント物質のドーパされる量が少なくなるという問題があった。

【0011】そこで、本発明は、上記の問題点に鑑みてなされたものであり、従来の炭素材料に比べて著しく大きな電気容量を有し、かつ充放電繰り返し特性の優れた電極及びその製造方法を提供することを目的とする。

【0012】

【課題を解決するための手段】上述の目的を達成するため、本願発明者は鋭意研究を重ねた結果、高度に配向した黒鉛構造を有する炭素(結晶性の高い炭素)ではなく、層状構造にわずかな乱層構造を持たせたもの、あるいは、選択的配向性を持たせた炭素を電極材料として用いることによって、電気容量が従来のものに比べて大きく、かつ、充放電繰り返し特性が優れた電極を得ることができるという知見を得ることができた。この炭素材料の乱層構造あるいは選択的配向性の程度を客観的に表す以下の通りとなる。

【0013】すなわち、X線回折法による炭素平面の層間隔が3.37Å~3.55Åのものであり、黒鉛のように鋭いピークを示すものではなく、かなり幅広い回折ピークを示すもの。

【0014】さらに、レーザーラマンスペクトルの1580cm⁻¹のピーク強度に対する1360cm⁻¹のピーク強度比が0.4以上1.0以下のものである。

【0015】それぞれの物性値は黒鉛化度を表す物性値として周知ではあるが、ラマン散乱から得られる物性値とX線回折から得られる物性値を組み合わせることにより材料の物性を表現できる。周知のように、ラマン散乱から得られる物性値とは炭素材料の表面から50nm程度の極表面の情報であり、X線回折から得られる物性値はその表面を含む数十μmぐらいのある程度の深さまでの平均としての情報である。つまり、この2つの物性値を組み合わせることにより深さ方向の構造が把握できるわけである。

【0016】また、回折ピークの半値幅から求めた結晶子の大きさは、(002)面の回折ピークからC軸方向の結晶子の大きさが20Å~1000Åのものであり、(110)面の回折ピークがほとんど現れないか、現れても非常にブロードであることからa b軸方向の結晶子の大きさが非常に小さいと認められるもの。なお、反射電子線回折パターンはブロードなリング状であり、結晶子が非常に細かいことを反映している。これらリングは黒鉛構造の(002)、(004)、(006)反射に相当する。また、各結晶子の包囲はランダムではなく、各結晶子の(001)面が特定の方向に揃っており、各結晶子間のC軸方向の相対的な傾きが±75度の範囲内のもの。

【0017】このように高黒鉛化炭素体に比べ面間隔が広く、結晶子の大きさが小さく、互いにある程度の配向性を有する炭素体が電極材料として良好な特性を示す。

【0018】以上の特性を有する炭素体は、例えば以下の製造方法によって得ることができる。すなわち、炭化水素又は炭化水素化合物を出発原料として、これを反応系へ供給し、基板上へ熱分解による気相堆積法により形成することができる。

【0019】炭化水素化合物としては炭化水素の一部に酸素、窒素、硫黄またはハロゲンより選択された少なくとも1つ以上の元素を含む特性基を付加または置換したものをを用いることができる。

【0020】上述の炭素材料をアルカリ金属等がドーパント物質として含有された電池の電極に用いると、従来の高黒鉛化炭素体に比べてドーパント物質のドーパ、脱ドーパが起こりやすく、電気容量が大きくなる。また、上述の炭素体は薄膜として基板上へ直接形成できるので、内部抵抗が小さく活物質の利用率が高くなる。また、任意の形状に作製できるので、電極の薄形化等が可能となるという効果がある。

【0021】

【発明の実施の形態】

(実施例1)以下、図面を参照して本発明を一実施例を挙げて詳細に説明する。

【0022】図1は、本願発明の電極に用いる炭素体のCuKαを光源とするX線回折図である。この回折ピークから次のブラッグの式(数1)

【0023】

【数1】

$$d = \frac{\lambda}{2 \cdot \sin \theta} \quad (\lambda = 1.5418 \text{ \AA})$$

【0024】により(002)面の平均面間隔を求めると3.45Åであり、ピーク半値幅βから次式(数2)

【0025】

【数2】

$$L_c = \frac{\kappa \cdot \lambda}{\beta \cdot \cos \theta} \quad (\lambda = 1.5418 \text{ \AA})$$

$$(\kappa = 0.9)$$

【0026】よりC軸方向の結晶子の大きさを求めると27.2Åであった。

【0027】また、図2はこの炭素体のアルゴンレーザを用いたラマンスペクトルである。この図から明らかなように1580cm⁻¹のピーク強度に対する1360cm⁻¹のピーク強度をみると0.8である。

【0028】また、反射高速電子線回折(RHEED)法で電子線の回折写真を求めると(002)、(004)、(006)反射はブロードなスポットを示しており、各結晶子の配向性はかなりよく、C軸方向の分布は±18度以内である。

【0029】この炭素体(炭素材料を基板上に形成した膜)を集電用ネットで挟持して電極とした。これを試験極Aとする。試験極Aを図3に示すような電解槽内に配設しリチウム金属を対極、リチウムをドーパント物質として、リチウム元素のドーパ・脱ドーパによる充放電試験を行った。図3において12は本願発明に係る炭素体よりなる電極(試験極A)、13是集電体、14は対極、15は参照電極として用いたリチウム、16は1モル過塩酸リチウムを溶解したプロピレンカーボネートからなる電解液、17は電解槽である。

【0030】図4は各種炭素材料にリチウムをドーパ・脱ドーパさせたときの25℃におけるリチウム参照電極に対する電位変化図である。図4の曲線Aは本願発明の電極の電位変化曲線である。曲線Aにおいて、電位が0Vに近づく方向がドーパ(充電)、高電圧になる方向が脱ドーパ(放電)である。

【0031】図5は各種炭素材料をリチウム参照電極に対し0Vから2.5Vの間で定電流により充放電させるテストにおける放電容量の変化を示す。図5の曲線Aは本願発明の電極特性を示す曲線である。この結果より明

らかなように、充本願の繰り返しによる容量劣化は殆ど無く繰り返し特性は非常に良好である。

【0032】以上のように、本願発明の炭素体を用いれば充放電可能な非水リチウム2次電池の負極を構成することができる。

【0033】以下に、上述の炭素材料の製造方法の一例を図面を用いて説明する。

【0034】図6は本願発明の電極に用いる炭素材料の製造に用いる炭素材料生成装置のブロック構成図である。

【0035】出発物質として使用される炭化水素及び一部に種々の特性基を含んだ炭化水素化合物として例えば脂肪族炭化水素好ましくは不飽和炭化水素、芳香族化合物、脂環式化合物がある。これらは1000℃で熱分解される。具体的にはアセチレン、ジフェニル、アセチレン、アクリロニトリル、1,2-ジブromoエチレン、2-ブチン、ベンゼン、トルエン、ピリジン、アニリン、フェノール、ジフェニル、アントラセン、ピレン、ヒキサメチルベンゼン、スチレン、アリルベンゼン、シクロヘキサン、ノルマルヘキサン、ピロール、チオフエン等

【0036】使用した炭化水素化合物の種類によって、後述する反応管への供給方法はバブラー法、蒸発法または昇昇法を用い毎時数ミリモル以下の供給量に制御される。供給量を多くするとスス状炭素堆積物が生成され、本発明の電極構成に必要な炭素材料は得られない。炭素材料が堆積、生成される基板は1000℃程度の反応温度で変質しないものである必要がある。

【0037】以下、製造工程に従って説明する。

【0038】真空蒸留による精製操作を行ったベンゼンが収納されたバブル容器1内にアルゴンガス制御系2よりアルゴンガスを供給してベンゼンをバブルさせ、パイレックスガラス管3を介して石英反応管4へベンゼン分子を給送する。この際バブル容器1内の液体ベンゼンの温度を一定に保持してアルゴンガス流量をバブル5で調節し、ベンゼン分子の反応管4内への供給量を毎時数ミリモルに制御する。一方、希釈ライン6よりアルゴンガスを流し、反応管4へ給送される直前のガラス管3内におけるアルゴンガス中のベンゼン分子数密度及び流速を最適化する。反応管4の外周囲には加熱炉8が設けられている。この加熱炉8によって反応管4内の堆積生成用基板は約1000℃の温度に保持されている。

【0039】ベンゼン分子が反応管4内に給送されるとベンゼン分子は反応管4内で熱分解し、基板上に炭素堆積物が生成される。反応管4内へのガスは排気パイプ9を介して排気系10へ導入され、反応管4から除去される。反応管4内に導入されたベンゼン分子は約1000℃の温度で加熱されて熱分解し、順次基板上に成長形成される。この場合成長される炭素は金属光沢を有した薄膜となり、従来のような製法により黒鉛材料を形成する

方法に比べ、低い温度で反応を進行させるため、良好な物質値をもつ炭素材料を製造することができる。なお、この方法であれば出発物質、出発物質の供給量、供給速度、反応温度を選定することにより、異方性等を任意に制御することができる。

【0040】(実施例2)第2の実施例の炭素膜の諸特性は以下の通りである。すなわち、(002)面の平均面間隔は図7に示す如く3.37Åであり、ラマンスペクトルによる1580cm⁻¹のピーク強度に対する1360cm⁻¹のピーク強度比は図8に示す如く0.50であった。また、反射高速電子線回折による各結晶子のc軸方向の分布は±60度以内であった。

【0041】基板上に形成したこの炭素膜からリード線を取り出して電極とし試験極Bとした。これを実施例1と同様な方法でリチウムをドーパント物質とし、ドーパ・脱ドーパによる充放電テストを行った。図4の曲線Bは本実施例による炭素材料の電位変化曲線である。また、図5の曲線Bは本実施例による炭素材料の繰り返しテストにおける放電容量の変化を示す。この結果より明らかな如く、放電容量、繰り返し特性とも非常に良好である。

【0042】なお、本実施例においては電解質に1モル過塩素酸リチウム、電解液にアロピレンカーボネートを用いたが、これに限定する必要はなく、その他の電解質として六フッ化硫酸リチウム、ホウフッ化リチウム、トリフルオロスルホン酸リチウム等があり、また電解液としてはジメチルスルフォキシド、ガンマブチラクトン、スルフォランテトラヒドロフラン、2-メチルテトラヒドロフラン、1,2-ジメトキシエタン、1,3-ジオキソラン等の有機溶媒や水があげられ、これらを単独もしくは混合して用いることができる。

【0043】(比較例1)石英基板上に1200℃で堆積させた炭素体を、基板より剥ぎ取った後2800℃で熱処理した黒鉛化炭素体について、本願発明を比較する。

【0044】図9にこの炭素体のX線回折データを示す。この炭素体の(002)面の面間隔は3.36Åであった。また、ラマンスペクトルにおいて1580cm⁻¹のピーク強度に対する1360cm⁻¹のピーク強度比は0.1であった(図10)。この炭素体を実施例1と同様な方法で電極とし試験極Cとした。試験極Cを図3に示すような電解槽内に配設し、実施例1と同様に充放電テストを行った。図4の曲線cは本比較例による炭素材料の電位変化曲線である。この結果より上記実施例1,2の電極に比べ、放電容量もわずかで、電極材料としては不適であった。

【0045】(比較例2)原油から揮発成分を除いた未精製の石油コークスを500℃で熱処理した。この炭素粉末体のX線回折図を図11に示す。この回折ピークより(002)面の平均面間隔は3.45Åであった。ま

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た、ラマンスペクトルにおいて 1580 cm^{-1} のピーク強度に対する 1360 cm^{-1} のピーク強度比は0.8であった。この結果を図12に示す。また反射高速電子線回折によりこの炭素体をプレスして得た電極における回折パターンによれば回折パターンの各リングが均一となり、配向性をもっていないことが判明した。この炭素体を発泡状ニッケル基板に充填し、プレスしたものを電極とし、試験極Dとした。試験極Dを図3に示すような電解槽内に配設し、実施例1と同様に充放電テストを行った。図4の曲線Dは本比較例による炭素材料の電位曲線である。この結果より上記実施例1、2に比べ放電容量は少ない。しかし初期充放電特性は比較例1に比べ、良好であった。

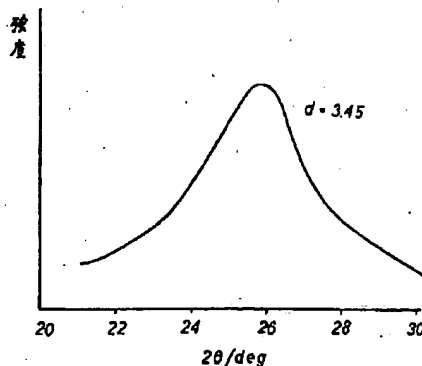
【0046】試験極Dを実施例1と同じ方法にて、充放電の繰り返しテストを行った。図5の曲線Dは本比較例による結果を示したものである。この結果より電極において各結晶子の配向性が全くないものは充放電の繰り返しにより容量の劣化が生じ、長期使用には耐え難いことが認められる。

【0047】

【発明の効果】本願発明によれば、従来の高黒鉛化炭素体に比べてドーパント物質のドーブ、脱ドーブが起こりやすく、電気容量が大きくなる。また、上述の炭素体は薄膜として基板上へ直接形成できるので、内部抵抗が小さく活物質の利用率高くなる。また、任意の形状に作製できるので、電極の薄形化等が可能となるという顕著な効果がある。

【図面の簡単な説明】

【図1】



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【図1】本発明の炭素材料のX線回折図である。

【図2】本発明の炭素材料のラマンスペクトルを示す図である。

【図3】本発明の炭素材料の電極特性測定のための装置の概略図である。

【図4】本発明の炭素材料及び既存の炭素材料の充放電特性図である。

【図5】本発明の炭素材料及び既存の炭素材料の充放電容量のサイクル特性図である。

10 【図6】本発明の一実施例の説明に供する炭素材料生成装置のブロック構成図である。

【図7】本発明の炭素材料のX線回折図である。

【図8】本発明の炭素材料のラマンスペクトルを示す図である。

【図9】既存の炭素材料のX線回折図である。

【図10】既存の炭素材料のラマンスペクトルを示す図である。

【図11】既存の炭素材料のX線回折図である。

20 【図12】既存の炭素材料のラマンスペクトルを示す図である。

【符号の説明】

12 試験極A

13 集電体

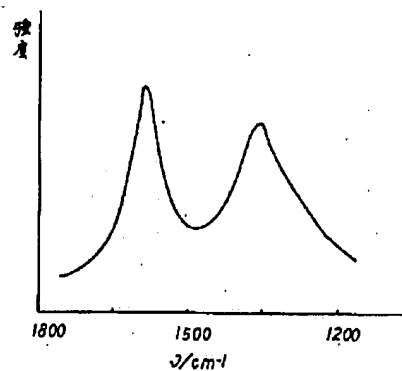
14 対極

15 参照極

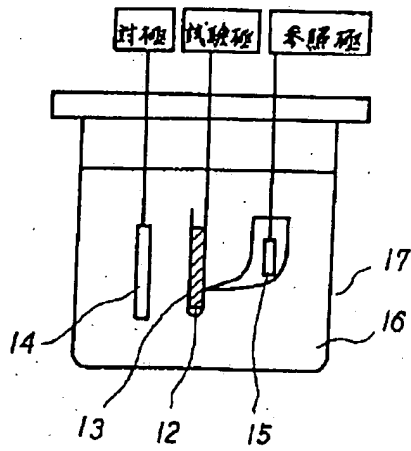
16 電解液

17 電解槽

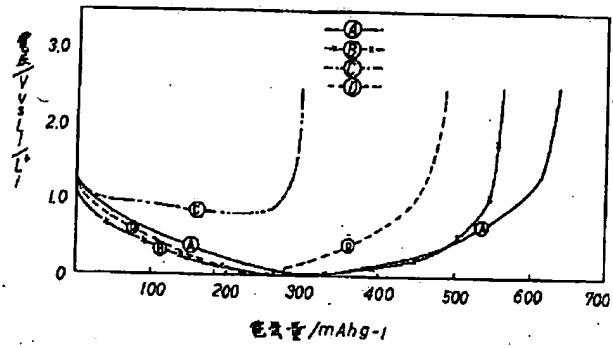
【図2】



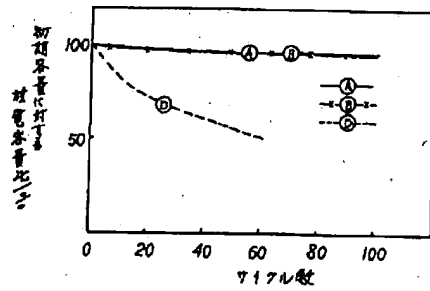
【図3】



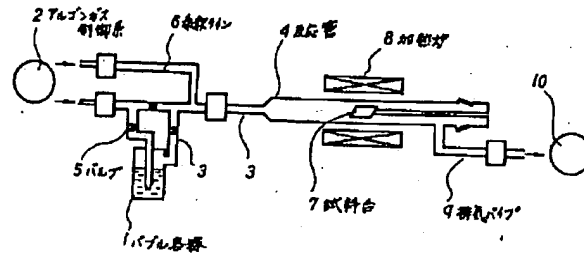
【図4】



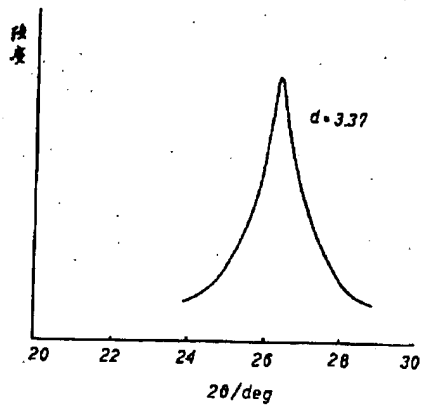
【図5】



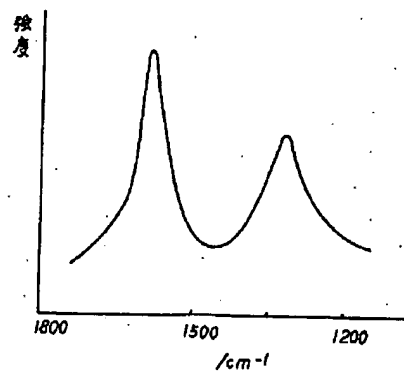
【図6】



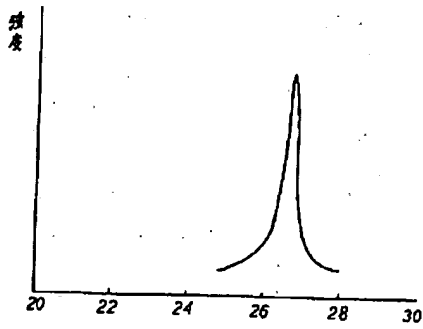
【図7】



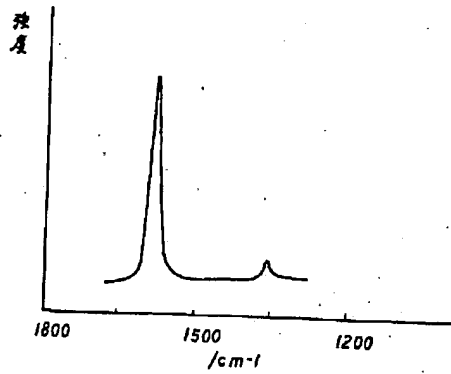
【図8】



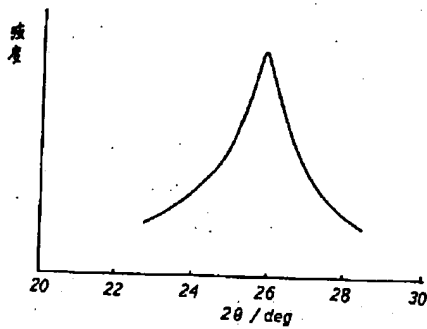
【図9】



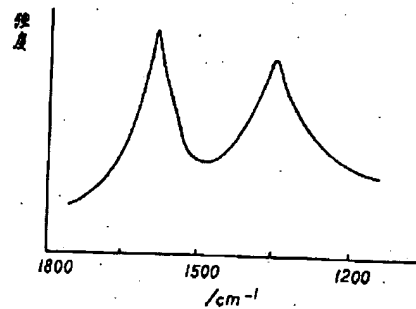
【図10】



【図11】



【図12】



フロントページの続き

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